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A STUDY OF THE STRUCTURE AND PROPERTIES  
OF CERTAIN ALUMINIDES

M. Ye. Drits, E. S. Kadaner, A. A. Vashchenko

Translation of "Issledovaniye struktury i svoystv nekotorykh alyuminidov". Legkie Splavy i Metody Ikh Obrabotki, (Light Alloys and Their Preparation), Edited by M.E. Drits, Moscow, "Nauka" Press, 1968, pp. 146-150.



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16. Abstract Experimental data are presented on the structure and heat resistance of the aluminides $ZrAl_3$ , $Fe_2Al_5$ and $Co_2Al_9$ , considering sp. wt., type of combination, and resistance to oxidn. at high temperatures. $Co_2Al_9$ possesses a relatively high heat of formation, attributed to its high heat-resistance characteristics.			
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## A STUDY OF THE STRUCTURE AND PROPERTIES OF CERTAIN ALUMINIDES

M. Ye. Drits, E. S. Kadaner, A. A. Vashchenko

The varied and valuable complex of physico-chemical /116\* properties possessed by metallic compounds has conditioned their possibility of practical application as materials having special physical properties, as well as the bases for structural heat-resistant alloys [1-7].

However, the application of such materials is for the most part inhibited due to the high brittleness of the metallides not only at room temperature, but also at elevated temperatures.

Outstanding in its properties among the metallic compounds is the class of aluminides, which are lightweight and have a relatively high melting point. Some of them are characterized by a high heat resistance and scaling resistance, and possess superconductive and other special physical properties. This class of metallides has not yet been sufficiently studied. The available data on the physical and mechanical properties are extremely limited and difficult to compare due to the differences in methods of producing and studying the compounds [8-10].

The goal of this work included the accumulation of experimental data on the structure and heat resistance of aluminides  $ZrAl_3$ ,  $Fe_2Al_5$ ,  $Co_2Al_9$ .

The available literary data on the properties of these compounds are presented below.

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Properties	ZrAl <sub>3</sub>	Fe <sub>2</sub> Al <sub>5</sub>	Co <sub>2</sub> Al <sub>9</sub>
Aluminum content, weight %.....	47.01	54.71	67.32
Fusion temperature, °C.....	1580	1173	946
Specific weight, g/cm <sup>3</sup> .....	4.11	--	3.46
Crystalline structure.....	Tetra- gonal	Monoclinic	Monoclinic
Character of compound formation..	Congruent	Congruent	By peritectic reaction
Heat of formation, kcal/mole.....	--	6.4	38.5
Electrical resistance, mkom.cm...	17	--	--
Microhardness at room temperature, kG/mm <sup>2</sup> .....	560	1000	735
Chemical stability.....	Resistant against oxidation	--	--
Solubility of ther elements in compound.....	--	--	High solubili of Fe, Ni, significant solubility of Si.

In selecting the indicated objects of study, consideration was also given to such characteristics as the specific weight, fusion temperature, character of compound formation, resistance to oxidation during heating and others, as well as to the practical interest which these compounds may have individually or as reinforcement phases in aluminum alloys.

The compounds ZrAl<sub>3</sub> and Fe<sub>2</sub>Al<sub>5</sub> have relatively high melting points, possess congruent melting points, and their specific weight is on the order of 4 g/cm<sup>3</sup>. The compound Co<sub>2</sub>Al<sub>9</sub> with specific weight of 3.46 g/cm<sup>3</sup> is formed according to the peritectic reaction. As compared with most other aluminides, compound Co<sub>2</sub>Al<sub>9</sub> differs in its high heat of

formation, which makes it possible to rely upon its high refractory characteristics.

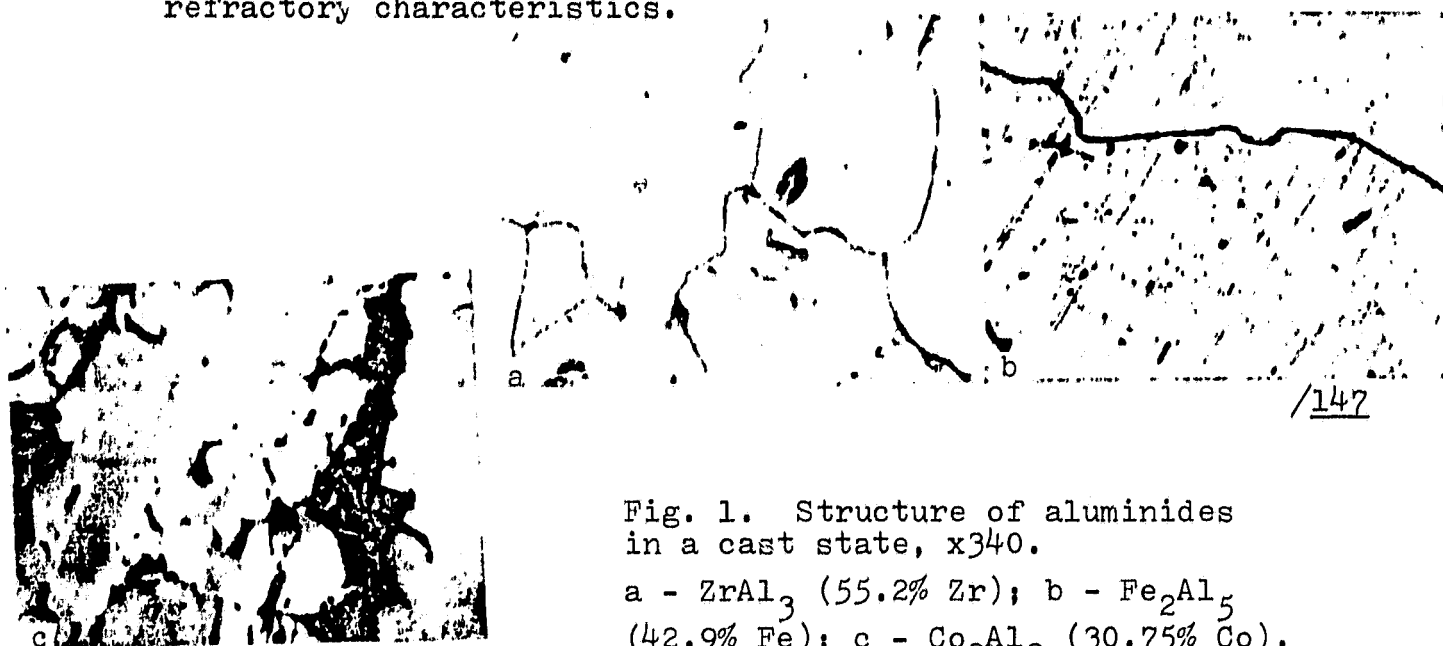


Fig. 1. Structure of aluminides in a cast state, x340.

a -  $\text{ZrAl}_3$  (55.2% Zr); b -  $\text{Fe}_2\text{Al}_5$  (42.9% Fe); c -  $\text{Co}_2\text{Al}_9$  (30.75% Co).

A study of the properties of the indicated metallic compounds is evidently good not only for clarifying their role as alloying elements in aluminum alloys, but also for an evaluation of their possible application as the basis for a heat-resistant alloy.

The preparation of the compounds selected for study was done by means of direct fusion of the pure components. The charge materials were: aluminum grade A99, iodide zirconium, armco-iron and cobalt grade KO. The computation of charge was conducted in accordance with the compound's stoichiometric composition. The compounds were prepared first in an arc furnace in a helium atmosphere in the form of lumps, and then smelted in an induction furnace under an argon stream with subsequent casting into a heated steel ingot mold with graphite fitting. The results of the chemical analysis indicated values close to the computational, with a deviation from the given composition within the margins of 1 - 1.5%.

Confirmed by means of metallographic analysis was the presence of a single-phase structure for compounds  $ZrAl_3$  and  $Fe_2Al_5$  (fig. 1). In the case of compound  $Co_2Al_9$ , however, despite the similarity of its chemical composition to the given one, the structure of the ingot was heterophasal, which is evidently associated with the peritectic character of formation of this compound.

Evident in the microphotograph (fig. 1,c) are thermo-etched sections of aluminum-cobalt eutectics and two types of crystals. Located inside the light-grey crystals are crystals with a darker coloration. In accordance with the character of peritectic transformations in the system Al - Co we may consider that the light-grey crystals are the compound  $Co_2Al_9$ , while the more cobalt-rich compound  $Co_4Al_{13}$  is located in the center.

For compounds  $ZrAl_3$  and  $Fe_2Al_5$ , an x-ray analysis was also conducted on a URS70 device in a RKD chamber with cobalt irradiation. The computation of the x-ray photographs to interplanar distances, the analysis of line intensities, and the comparison of the results with tabulated /148 values for pure substances showed that the crystalline structure of the studied materials corresponds to the structure of compounds  $ZrAl_3$  and  $Fe_2Al_5$ .

For the purpose of eliminating defects in the cast structure and increasing the plasticity of the brittle compounds, hot deformation of the cast ingots was performed. Efforts were made by means of the deformation also to accelerate and facilitate the diffusional processes of equalization in compound  $Co_2Al_9$  with the peritectic structure by subsequent high-temperature annealing. The deformation of the cast compounds was implemented by means of static hot jumping up on a hydraulic press of 200 t. The excess part of the ingot with concentrated piping was cut off

by the electric spark method, while the healthy part of the ingot 25 mm in diameter and 40 mm in height was placed in a steel casing in the form of a cup, which was sealed at the top with a cover. The ingots in the casing were heated to  $600^{\circ}$ , after which they were upset by 50-60%. The press instrument was heated to  $500^{\circ}$ . The selected conditions made it possible to perform deformation of the indicated compounds practically without cracking and disintegration.

The changes in the microstructure after deformation were expressed in the appearance of slippage lines within the grains and the pulverization of individual grains. In the case of fusion of compound  $\text{Co}_2\text{Al}_9$  after deformation, the traits of the cast dendritic structure are strongly retained.

An evaluation of the comparative heat resistance of the studied compounds was conducted on deformed samples by the long-time hardness method within the temperature sphere of  $500 - 700^{\circ}$ . Used for this purpose was a device with lever loading mechanism. The hardness measurement was done with a 5 mm diameter ball under a load of 150 kg and with holding the sample under load for a period of 1 hr. Testing up to  $600^{\circ}$  was conducted in a medium of molten saltpetre, and at higher temperatures -- in an air environment. At room temperature the hardness was measured on a Brinell press with a 5 mm ball under load of 250 kg on the samples which had previously been tested at elevated temperatures. The phase microhardness measurements were conducted on cast samples on an IMT-3 device at a load of 20 and 50 g.

Based on the example of compounds  $\text{Fe}_2\text{Al}_5$  and  $\text{Co}_2\text{Al}_9$ , the effect of high-temperature annealing on their structure and hardness at increased temperatures was studied. The samples were annealed in vacuum and argon-filled quartz ampules at  $1000^{\circ}$  for 100 hrs. for compound  $\text{Fe}_2\text{Al}_5$  and at  $640^{\circ}$  -- 10 hrs +  $880^{\circ}$  -- 100 and 380 hrs. for the compound  $\text{Co}_2\text{Al}_9$ .



Presented below are the data for measurement of micro-hardness and hardness of the studied compounds:

Compound.....	ZrAl <sub>3</sub>	Fe <sub>2</sub> Al <sub>5</sub>	Co <sub>2</sub> Al <sub>9</sub>
H <sub>μ</sub> (P = 50g), kl'/mm <sup>2</sup> .....	590	1100	750
H <sub>B</sub> (P = 250 kg), kl'/mm <sup>2</sup> .....	216	264	244

In a cast state, all the compounds are very brittle and are characterized by high microhardness values. After conducting the hot deformation, it was possible to perform standard hardness tests after Brinell at a load of 250 kl'. The imprints for hardness had a regular form without any traces of cracks. The hardness value of the compounds in a hot deformed state is considerably lower as compared with the microhardness of the cast samples, which is evidently associated to a certain degree with the increased plasticity of the compounds as a result of the deformation.

The change in long-time hardness of compounds ZrAl<sub>3</sub> and Fe<sub>2</sub>Al<sub>5</sub> depending on the test temperature is presented in fig. 2. In a deformed state (curves 1,2), the highest values /149 of long-time hardness within the entire range of test temperatures is exhibited by the high-melt compound ZrAl<sub>3</sub>. In the temperature interval of 550 - 650° this compound suffers practically no loss of strength. Its hardness comprises around 60 - 70 kg/mm<sup>2</sup>. Compound Fe<sub>2</sub>Al<sub>5</sub> has a noticeable loss of strength with increased test temperature, and at a temperature of 600° already yields significantly by its value of long-time hardness to compound ZrAl<sub>3</sub>. Annealing the compound Fe<sub>2</sub>Al<sub>5</sub> leads to an increase in its long-time hardness (curve) only at 500°. At test temperatures of 550 - 600°, the long-time hardness of the compound before and after annealing is practically identical. An increase in the long-time hardness of compound Fe<sub>2</sub>Al<sub>5</sub> at 500° due to annealing is evidently conditioned by the high stability

of the recrystallized structure of the annealed material as compared with its deformed state (fig. 3,a).

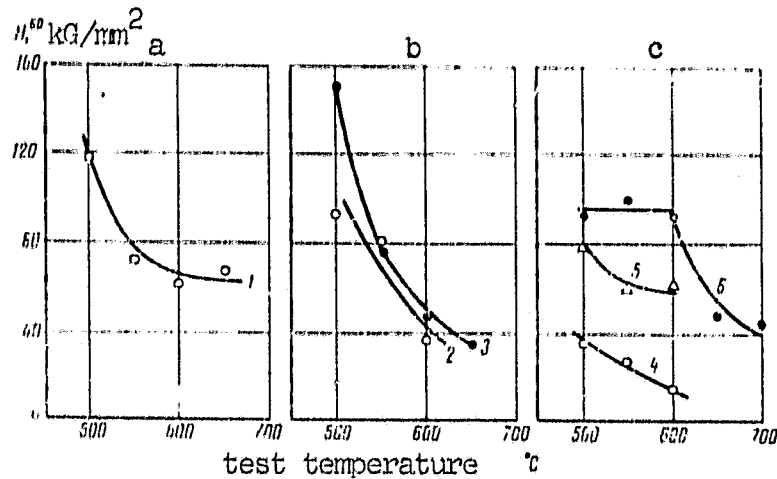


Fig. 2. Long-time hardness of aluminides at various temperatures.

a -  $ZrAl_3$ ; b -  $Fe_2Al_5$ ; c -  $Co_2Al_9$ .

1 - heat deformed; 2 - heat deformed; 3 - heat deformed and annealed at  $1000^\circ$  -- 100 hrs; 4 - heat deformed; 5 - heat deformed and annealed at  $880^\circ$  -- 100 hrs.; 6 - heat deformed and annealed at  $880^\circ$  -- 380 hrs.

The alloy corresponding in its chemical composition to compound  $Co_2Al_9$ , as indicated above, has a heterophase structure and in a non-annealed state is characterized by very low values of long-time hardness. At  $500^\circ$  the long-time hardness of the Al-Co alloy is equal to  $40 \text{ kg/mm}^2$ , and at  $600^\circ$  it drops to  $17 \text{ kg/mm}^2$  (fig. 2, curve 4). As a result of annealing this alloy at  $640^\circ$  for 10 hrs., the eutectic areas disappear in its structure. Subsequent high-temperature annealing at  $880^\circ$  for a period of 100 hrs. still does not lead to a full homogenization in the structure of the alloy, which remains two-phased. (fig. 3,b). However, after the indicated thermal processing there is observed a

noticeable increase in the long-time hardness (see fig. 2, curve 5). At a test temperature of  $500^{\circ}$ , the long-time hardness of the Al-Co alloy is approximately doubled, while at  $600^{\circ}$  it is increased by approximately 3 times and becomes close to the long-time hardness for compound  $ZrAl_3$ . Longer annealing at  $880^{\circ}$  for a period of 380 hours leads to full completion of the peritectic transformation and to an achievement of a single-phase, homogeneous structure of the compound  $Co_2Al_9$  (fig. 3,c). The compound  $Co_2Al_9$  obtained by this means is characterized by high values of long-time hardness (around  $100 \text{ kg/mm}^2$ ) and suffers practically no loss of strength in the temperature interval of  $500 - 600^{\circ}$  (see fig. 2, curve 6). At a test temperature of  $600^{\circ}$ , the long-time hardness of the compound  $Co_2Al_9$  is 50% higher than for compound  $ZrAl_3$ , and 170% higher than for compound  $Fe_2Al_5$ .

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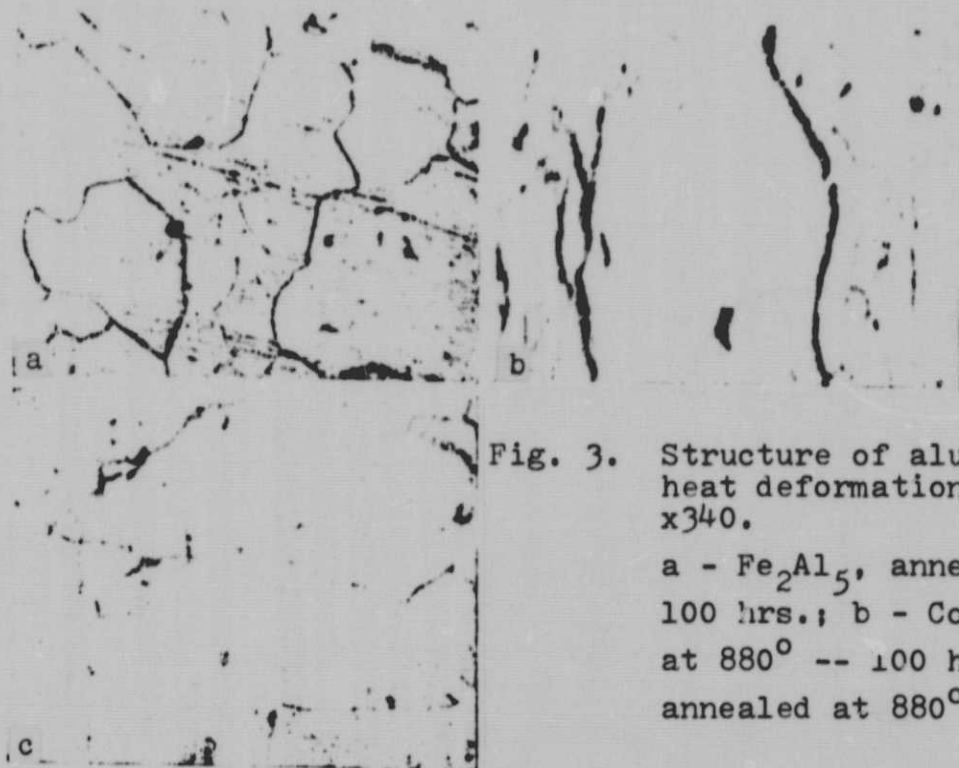


Fig. 3. Structure of aluminides after heat deformation and annealing, x340.

a -  $Fe_2Al_5$ , annealed at  $1000^{\circ}$  - 100 hrs.; b -  $Co_2Al_9$ , annealed at  $880^{\circ}$  -- 100 hrs.; c -  $Co_2Al_9$  annealed at  $880^{\circ}$  -- 380 hrs.

As compared with a heterophasal alloy of the same composition, compound  $\text{Co}_2\text{Al}_9$  has significantly better resistance to the action of temperature and stress, which is particularly apparent at high test temperatures. Thus, at  $600^\circ$  the long-time hardness of compound  $\text{Co}_2\text{Al}_9$  is 6 times higher than that of an Al-Co alloy of the same chemical composition.

Only at temperatures above  $600^\circ$  is there a noticeable loss of strength in the cobalt aluminide. At test temperatures of  $650 - 700^\circ$ , the compound  $\text{Co}_2\text{Al}_9$  yields in its long-time hardness to compound  $\text{ZrAl}_3$ , but exceeds compound  $\text{Fe}_2\text{Al}_5$ .

Thus, the comparative evaluation of heat resistant aluminides which we have conducted has shown that the highest and most stable hardness values are possessed by compound  $\text{Co}_2\text{Al}_9$ . The high absolute values of long-time hardness and the low degree of strength loss for aluminide  $\text{Co}_2\text{Al}_9$  at increased temperatures allow us to conclude that cobalt must have a positive effect on the heat resistance of aluminum alloys.

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